ELSEVIER

Chemical Engineering Journal 134 (2007) 239–245

Chemical Engineering Journal

www.elsevier.com/locate/cej

Oxygenated additives production for diesel engine emission improvement

F. Frusteri [a,*], L. Spadaro [a], C. Beatrice [b], C. Guido [b]

[a] *Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano" (CNR-ITAE), Via Salita S. Lucia sopra Contesse n. 5, I-98126 Messina, Italy*
[b] *Istituto Motori-Consiglio Nazionale delle Ricerche, Naples, Italy*

Abstract

This present paper evaluates the potentiality in terms of production method and pollutant emission reduction of a new bio-derived oxygenated compound, 1,1-diethoxyethane, used as additive in an automotive diesel engine. The additive is obtainable from bio-ethanol by means of an acid-catalysed process. Several acid ion-exchanged polymers with acidic strength comparable with that of "concentrated" sulphuric acid were used to prepare silica-*heterogenized* perfluorosulfonic (PFS) acid catalysts by incipient wetness impregnation of commercial silica samples. The acid catalysts were used in the synthesis of acetal at 4 °C and 3 atm in a stirred batch reactor. A systematic comparison of reaction path and catalysts acid-strength points to a direct relationship between *acidic capacity* and *catalytic* activity.

The product has good characteristics for diesel blending, but it is characterized by a low flash point. The evaluation of the additive performance in a diesel fuel blend was carried out in a passenger car light-duty diesel engine in two steady-state operation points. The chosen testing points are considered partially representative of the engine behaviour during the NEDC test procedure.

Engine tests showed an insensitive effect of 1,1-diethoxyethane on gaseous pollutant emissions (HC, CO and NOx), on the contrary a marked reduction of exhaust smoke was verified. Fuel consumption was slightly increased because of the total oxygen content of the blend.

Keywords: Acetal synthesis; Bio-derivable oxygenated fuels; Diesel engines emission reduction

1. Introduction

The growing need to reduce the environmental impact of the modern lifestyle imposes a continuous development of novel technologies aimed at a severe reduction of pollutant emissions, mainly from mobile sources, to ensure a tolerable quality of life in metropolitan areas. This has involved in the last years an extraordinary research effort for disclosing and synthesizing more effective and cleaner fuels that could result in lower CO_2 and pollutant emissions. In perspective, a way to such goal is represented by increasing the use of natural energy sources, like biomass, instead of fossil fuel.

As well known, ethanol is considered a clean bio-derivable additive (from biomass) for diesel fuels [1]. However, some disadvantages in its use should be overcome, mainly the strong instability of the ethanol–diesel fuel blend even at low temperature. An alternative to ethanol as bio-derivable additive for diesel fuel could be the 1,1-diethoxyethane (also named "*acetal*") produced by the acid-catalysed addition of ethanol and acetaldehyde [2]. This compound is miscible in diesel fuel and shows good characteristics in terms of viscosity and auto-ignition temperature, as reported in Table 1.

Generally, *"acetal"* is industrially produced *via* uneconomic homogeneous catalytic process, involving the reaction of two moles of ethanol with one of acetaldehyde to produce one mole of acetal. Like many other *high-value* chemical syntheses, this process still industrially lies on the use of strong mineral acids, such as H_2SO_4 or HF, as catalysts [3]. Clearly, environmental and economic reasons [4,5] impose the adoption of cleaner and more selective process technologies deserving the replacement of homogeneous processes with safer heterogeneous catalytic technologies based on the employment of strong solid-acid catalysts [6]. Although zeolites and functionalized silica (by addition of sulfonic acid groups) were found to catalyze many organic reactions [7–15], only few articles have addressed the use of stable and selective solid-acid catalysts for the acetal manufacture instead of mineral acids [16,2]. On the other hand, the feasibility of the acetal synthesis through the employment of catalytic heterogeneous systems has been documented [2], yet the targets were longer inadequate for industrial purposes [16,2].

---

* Corresponding author. Tel.: +39 090 624233; fax: +39 090 624247.
E-mail address: francesco.frusteri@itae.cnr.it (F. Frusteri).

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.03.042

Table 1
Main properties of acetal

Molecular formula	$C_6H_{14}O_2$
Density (g/ml at 25 °C)	0.831
Boiling point (°C)	103
Melting point (°C)	−100
Relative density (diesel fuel)	≈1
Solubility in water (g/100 ml)	5.0
Vapour pressure (kPa at 20 °C)	2.7
Relative vapour density (air = 1)	4.1
Flash point (°C)	−21
Auto-ignition temperature (°C)	230
Explosive limits (vol% in air)	1.6–10.4

Table 2
List of the studied catalysts

Code	Polymer[a] (wt.%)	μeq. H^+ g^{-1}[b]	SA_{BET} (m^2 g^{-1})	Mean pore diameter (Å)
6A-LM50	6.0	73	120	198
13A-LM50	13.0	154	113	176
18A-LM50	18.0	185	107	146
24A-LM50	24.0	283	99	132
30A-LM50	30.0	354	95	129

[a] Polymer loading evaluated by TGA analysis.

[b] Brönsted's acidity evaluated by ZPC analysis.

Moreover, probing a series of different acidic systems (zeolite, modified clay and sulfonic ion-exchange resins), Capeletti et al. did not observe "a clear relationships between activity and the amount of acidity, or the physical properties of the catalysts" [2].

Amongst various classes of potential solid-acid catalysts, in recent years a great interest has been focused on acid ion-exchanged polymers, such as Nafion®, characterized by terminal sulfonic groups, whose acidic strength is comparable with that of "concentrated" sulphuric acid [17,18]. However, the use of "pure" perfluorosulfonic-like solid-acids are generally limited by an intrinsic low surface exposure reflecting in poor process yields [19].

Therefore, this paper is aimed at assessing synthesis route and catalytic performance of silica-heterogenized perfluorosulfonic (PFS) acids in the synthesis of acetal and at evaluating the emission reduction performance on the use of acetal in a diesel fuel. On this account, tests on a modern light-duty diesel engine were performed comparing a standard European high quality diesel fuel with its blend with 1,1-diethoxyethane.

2. Experimental

2.1. Catalysts

Differently loaded (6–30 wt.%) acid perfluorosulfonic–*silica* catalysts (PFS–*SiO_2*) were prepared by the incipient wetness impregnation of a commercial silica sample with a solution of PFS-polymer, according to the following procedures. The catalysts were prepared by the stepwise addition of hydroalcoholic solution of PFS-polymer (*A-type*, 5 wt.%) to a commercial SiO_2 powders (*Fumed silica*, "*LM*-50", *Cab-O-Sil division*). Before the impregnation the *SiO_2* support was treated in air at 300 °C, while the solution of copolymer was further diluted in ethanol (1:4). Then, the solution was added to *SiO_2* support until visible wetness was obtained. Subsequently, the material was dried at 60 °C for 30 min. This procedure was repeated until the designed amount of polymer was loaded on the support. After deposition, all the samples were treated in air at 120 °C for 2 h.

The amount of PFS-polymer was determined by TGA–DSC measurements using a *NETZSCH Simultaneous Thermal Analysis Instrument STA 409 C*. Analysis of powdered catalysts was carried out using a *Philips X-Pert* diffractometer operating with Cu Kα radiation (1.5405 Å) at 40 kV and 30 mA. Modelling of XRD spectra has been performed by deconvolution analysis of experimental profiles by a linear combination of Gaussian components, using the "*PeakFit v*4" software package (*Jandel Scientific*) [20]. Scanning electron microscopy (SEM) analyses have been carried out using a *Jeol* 5600 *LV* microscope, operating with an accelerating voltage of 20 kV. The SEM micrographs have been taken after samples coating by gold sputtering. The Brönsted acidity was estimated electrochemically by the zero point charge (ZPC) technique, according to the procedure elsewhere described in [21]. Testing in the acetal synthesis was performed at 4 °C and a pressure of 3 atm using a 100 cm^3 batch reactor containing 0.05 g of catalyst and 60 cm^3 of a reactant mixture of acetaldehyde/ethanol in the molar ratio 1:2, stirred at 2000 rpm. Reagents and products were analysed using a *HP* 5890 gas chromatograph.

The list of the studied catalyst is reported in Table 2.

2.2. Definition of the tested fuel blend

The preliminary evaluation of diesel/acetal blend advantages with respect to the use of the pure diesel fuel was carried out for only one percentage blend. The choice of the percentage blend was evaluated on the base of preliminary analysis in order to estimate the better compromise between the flash point reduction and the oxygen content increment in the blend.

Table 3
Main properties of the reference diesel fuel

Fuel chemical–physical property	
Density at 15 °C (g/l)	833.7
Kinematic viscosity at 40 °C	2.9
IBP (°C)	185.9
90% volume (°C)	334.1
FBP (°C)	361.4
Heat of combustion (MJ/kg)	43.0
Formulation of fuel	
Paraffins (wt.%)	40.7
Naphten (wt.%)	39.5
Aromatics (wt.%)	22.0
Oxygen (wt.%)	0.0
Sulphur (mg/kg)	31.0
Cetane number	53.3

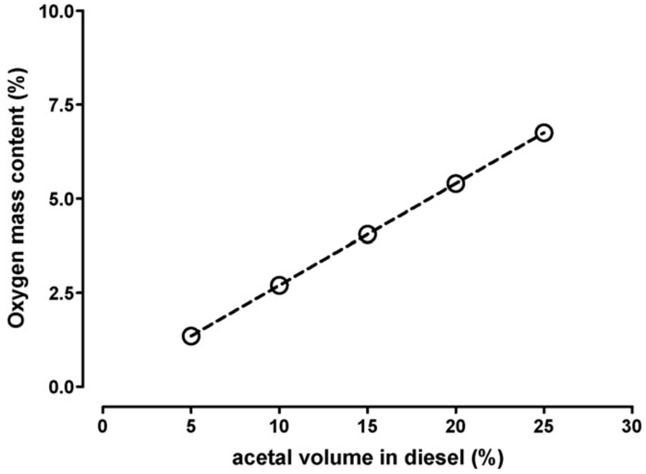

Fig. 1. Mass oxygen content of the acetal/diesel fuel blend vs. the acetal volume percentage.

As reference diesel fuel a high quality low sulphur diesel fuel was selected. The fuel respects the 2005 European regulations and its specifics are reported in Table 3.

From past experiences on oxygenated additives for diesel emission reduction [22,23], it was evidenced that emission reduction, and in particular exhaust smoke abatement, depend upon the fuel oxygen content and in any case, the threshold for an effective smoke reduction is about at least 3% in mass of oxygen.

In Fig. 1, the oxygen mass content versus acetal volume in the base fuel is plotted. To reach the indicated threshold oxygen content a blend in volume of about 10% of acetal and 90% of diesel is necessary.

Therefore, a blend of 10% was considered as the starting fuel blend for the emission analysis.

In order to evaluate the flash point decrease with the addition of acetal to diesel fuel, a determination of the flash point for three selected blends at 5, 10 and 20% was also performed. The results are reported in Table 4.

All blends are below the European regulation limit (52 °C). However, as above considered, this result does not weaken the interest on this kind of product as useful additive for emission reduction. In any case, the blend tested in the engine (10% acetal in 90% diesel) shows a flash point of 32 °C.

Table 4
Flash point for the acetal/diesel fuel blends

Fuels	[a]Flash point (°C)
100% diesel fuel	73
5% acetal/95% diesel fuel	45
10% acetal/90% diesel fuel	32
20% acetal/80% diesel fuel	28

[a] Evaluated on the basis of ASTM (D93/02) normative.

The selected blend was tested in a diesel engine and compared with the pure base fuel in terms of engine performance and exhaust emissions.

3. Results and discussions

3.1. Characterization and tests of the catalysts

3.1.1. Structural properties

As summarised in Table 2, all incipient catalysts features an almost similar *surface area* (SA_{BET}), ranging from ca. 90 to 120 m^2 g^{-1}, and *pore size distribution*, characterized by the marked presence of micro-mesopores with an average diameter fairly depending on the loading and ranging from ca. 130 to 200 Å.

The XRD patterns of high loaded catalyst (30A-LM50) and of bare PSF-*polymer* (obtained by slow evaporation of solvent) are compared in Fig. 2A. Namely, the catalyst displays rather broad and poorly resolved XRD lines in 2θ range 10–45°, characterized by two more or less resolved maxima likely related to the polymeric chains [20] and to the amorphous phase of silica ($2\theta = 21.5°$). While the unsupported copolymer features a rather symmetric XRD peak in the 2θ range 10–20° coming from the convoluted signals of amorphous ($2\theta = 16.0°$) and crystalline ($2\theta = 17.5°$) polyfluorocarbon phase. Then, the deconvolution analysis of the X-ray diffractograms, shown in Fig. 2B, indicates that for the 30A-LM50 catalyst the ratio between the peak area of crystalline and amorphous phases ("c/a" of ca. 0.54) is markedly lesser than for unsupported copolymer (equal to 0.91). The lower

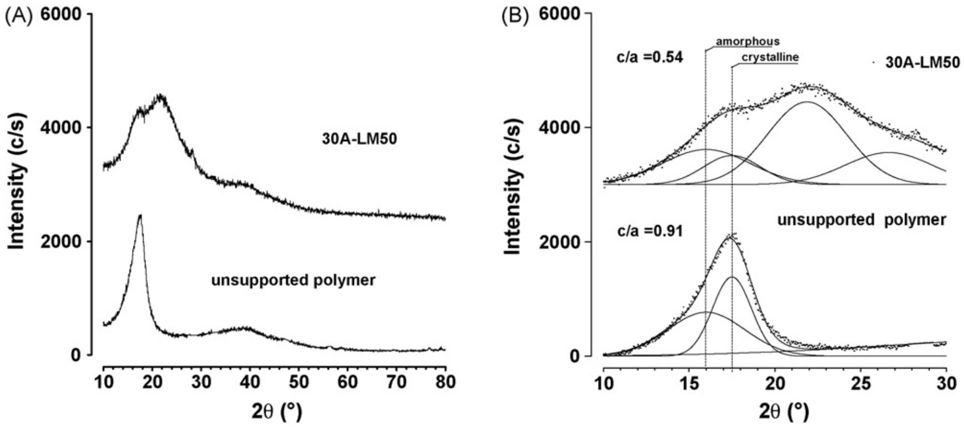

Fig. 2. X-ray diffraction patterns (A) and relative deconvolution analysis (B) of catalyst 30A-LM50 and reference unsupported PSF-polymer.

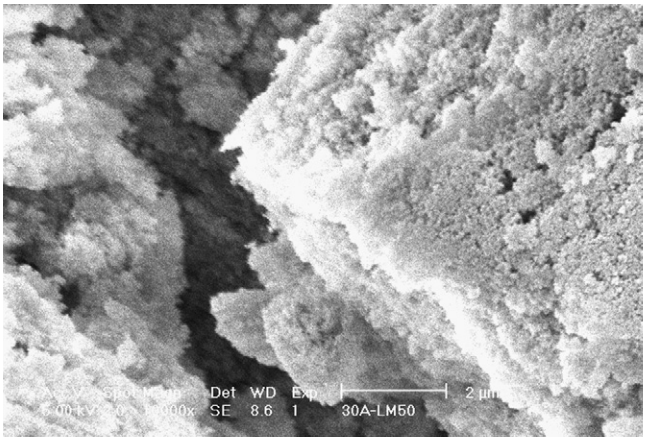

Fig. 3. SEM pictures of samples 30A-LM50 at 10K× of magnification.

grade of PFS-crystallinity observed in the catalysts proves the strong interaction created between the polymeric phase and the inorganic carrier oxide, pointing to a direct role of the textural properties of the SiO_2 support (e.g., abundance and volume of micropores) that may affect the features of the perfluorosulfonic chain [24–26]. In particular Fig. 2B documents that the process of "anchoring" modifies the amorphous/crystalline arrangement of PFS chains, leading to a greater amorphous character at which corresponds a higher hydrophilic behaviour of the polymeric phase.

The SEM image of sample 30A-LM50 is shown in Fig. 3. As can be noticed, this sample is characterized by the presence of regular structure consisting of aggregates with an average size of ca. 20 μm. Moreover, from the SEM image (Fig. 3) emerges that for the used support the value of 30% represents the upper limit of loading after the which the supporting process is not advantageous due to the incipient "over-saturation" of pores with consequent growth of multi-layer of PFS phase.

3.1.2. Acidic properties

The data relative to the acidic capacity of the various catalysts are summarised in Table 2 in term of proton (H^+) per gram of catalyst (μeq. $H^+ g^{-1}$). The ZPC measurements indicate the presence of an "abundant" Brönsted's acidity related to the structure property of polymers and silica carriers. Namely, all the studied systems possess an acidic capacity ranging from 70 to 350 μequiv. $H^+ g^{-1}$, closely dependent on the amount of polymer. In fact, considering the effects of loading on the acid capacity of *type*-A/LM50-*SiO*$_2$ systems, an almost linear rise of the acidity with the polymer loading is observed in the whole range (6–30 wt.%) investigated, as shown in Fig. 4. These findings are not so obvious considering that the replacement of strong liquid mineral acids (HCl, H_2SO_4, etc.), with solid ones, imply some differences such as the fact that in a homogeneous system an increase in acid's amount leads, in the right range, to a "linear rising" in system's Brönsted acidity, otherwise, for heterogenized system an increasing in polymer loading not always has a similar effect. Heterogeneous systems are in this case characterized by sulfonic acid groups (on polymer's short-lateral-chains) those are at different levels in contact with the carrier's surface. In this sense [–SO_3H] groups may differently interact with the surface of silica. Therefore, the support could induce some effect (through the formation of H-bonds) on proton mobility and/or interferes with the mass transfer diffusion phenomena, also diversely limiting the protons mobility. In other words, the modes through the PFS phases are anchored could lead to a different acid-strength for the diversely loaded heterogenized catalysts, observable in a "*alkaline-wake* ambient" as the reaction medium. In this sense, superior protons mobility will drive to higher performance in the synthesis of acetal.

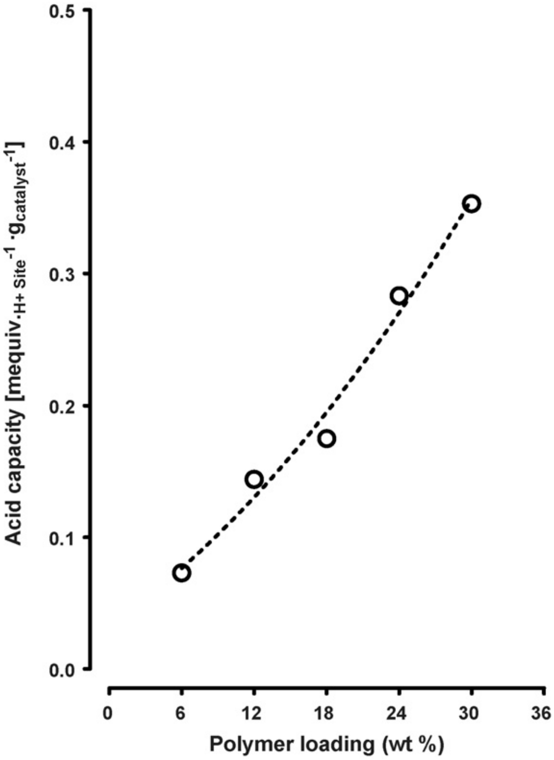

Fig. 4. Relationship between acidic capacity of various catalysts and polymer loading.

3.1.3. Catalytic activity

The catalytic synthesis of acetal in the presence of PFS-*SiO*$_2$ systems leads to the exclusive formation of acetal. No traces of PFS in the reacting solution, due to leaching phenomena, were detected. Activity data at 30 min of reaction time, using a catalyst/reagents ratio of 1/900 (wt/wt), are summarised in Table 5 and Fig. 5, in terms of conversion of ethanol (X_{ethanol}, %), acetal productivity ($\mathrm{mol\,h^{-1}\,g_{cat}^{-1}\,l_{slurry}^{-1}}$) and site time yield ($\mathrm{mol\,h^{-1}\,meq.^{-1}_{H^+\,site}\,l^{-1}_{slurry}}$).

As a rule, the conversion increases with the acidity of catalysts (Table 5) in right agreement with a higher Brönsted's acid capacity (Table 2), although for the studied catalysts Brönsted acidity measurements were carried out through an aqueous solution (NaCl/water solution), while the reaction medium is represented by an anhydrous solution of ethanol/acetaldehyde characterized by different acid–base behaviour and very low "ionic driving force".

Table 5
Catalytic activity data carried out at 4 °C and 3 bar and at 30 min of reaction time

Catalysts	X_{ethanol} (%)	Acetal productivity ($\mathrm{mol\,h^{-1}\,g_{cat}^{-1}\,l_{slurry}^{-1}}$)	Site time yield ($\mathrm{mol\,h^{-1}\,meq._{H^+\,site}^{-1}\,l_{slurry}^{-1}}$)
6A-LM50	5.1	5.9	80.8
12A-LM50	11.0	13.1	85.1
18A-LM50	14.2	16.1	87.0
24A-LM50	21.8	26.1	92.2
30A-LM50	28.9	35.6	98.6

A superior catalytic performance is found for the catalyst with higher loading (30%) of acid polymer, denoted by the highest ethanol conversion (ca. 30%) and acetaldehyde productivity (ca. 36 mol $\mathrm{h^{-1}\,g_{cat}^{-1}\,l_{slurry}^{-1}}$). Anyway, the nature of the SiO_2 support plays also a role on the catalytic performance of the various samples. In particular, the difference in site time yield (STY) value (Table 5), point to a direct role of the SiO_2 support that at lower PFS loading effects limiting the protons mobility of the sulfonic acid groups. Then, far away from equilibrium conditions, the reaction kinetics depend almost linearly upon the Brönsted acidity according to an almost *straight*-line increase in acetal productivity with the polymer loading, as shown in Fig. 5. These findings suggest that Capeletti et al. did not observe "a clear relationships between activity and the amount of acidity or the physical properties of the catalysts", because the authors have probed chemical–physical different systems [2].

In all experiments carried out no side products were detected, then selectivity was considered always 100% to acetal.

Although the ethanol conversion is limited by thermodynamic constraints due to water formation:

$$2C_2H_5OH + CH_3CHO \leftrightarrows (C_2H_5O)CHCH_3 + H_2O$$

however, the maximum acetal productivity value (ca. 36 mol $\mathrm{h^{-1}\,g_{cat}^{-1}\,l_{slurry}^{-1}}$) is remarkable, resulting higher by ca. two orders of magnitude than those recently reported in the literature using diverse solid-acid catalysts for acetal systems [2].

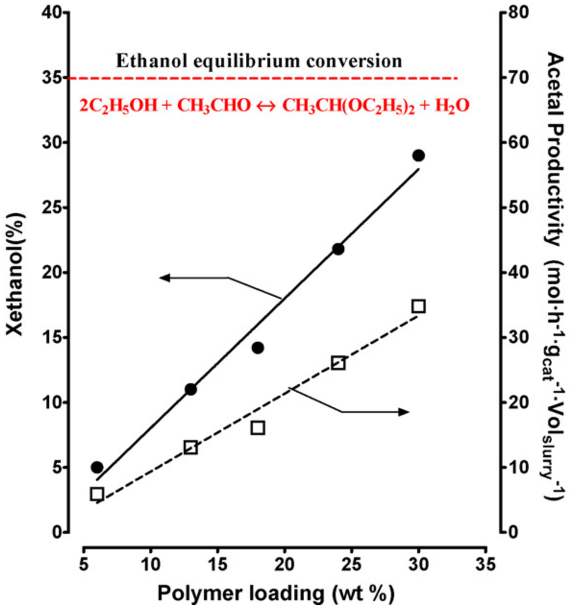

Fig. 5. Synthesis of acetal at 4 °C and 3 atm. Ethanol conversion and acetal productivity of various catalysts vs. polymer loading.

3.2. Engine performance with diesel/acetal blend

Generally, the analysis of engine performance are done by means of the study of the behaviour of cylinder pressure, injector control signal and the rate of the heat release of combustion, this last calculated from the cylinder pressure data [27].

The engine tests were done at the same speed equal to 1500 revolution per minute (rpm) in two different torque values: 2 and 5 bar of brake mean effective pressure (BMEP).

In Figs. 6 and 7 the energizing current of the electro-injector (signal of the injection command), the cylinder pressure, the rate

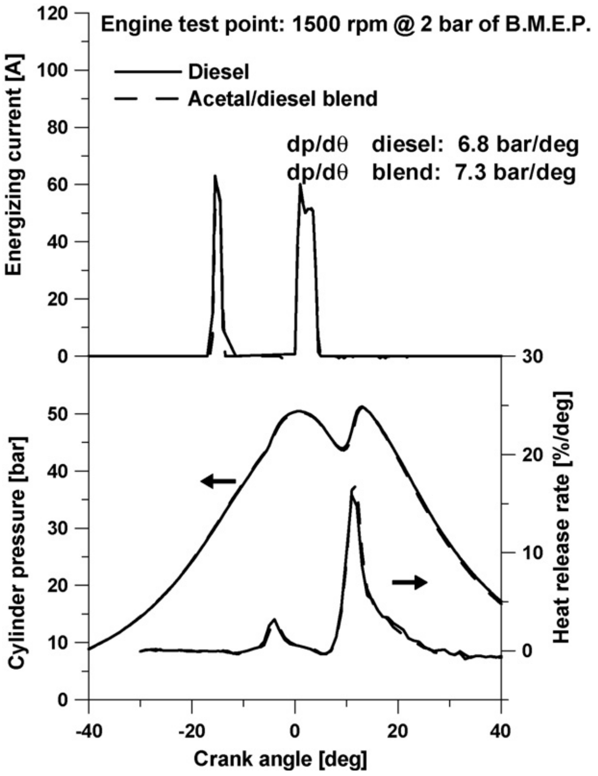

Fig. 6. Energizing current of electro-injector, cylinder pressure, rate of heat release of combustion and dp/dϑ comparison for the two fuels in the 1500 rpm at 2 bar of BMEP engine operating point.

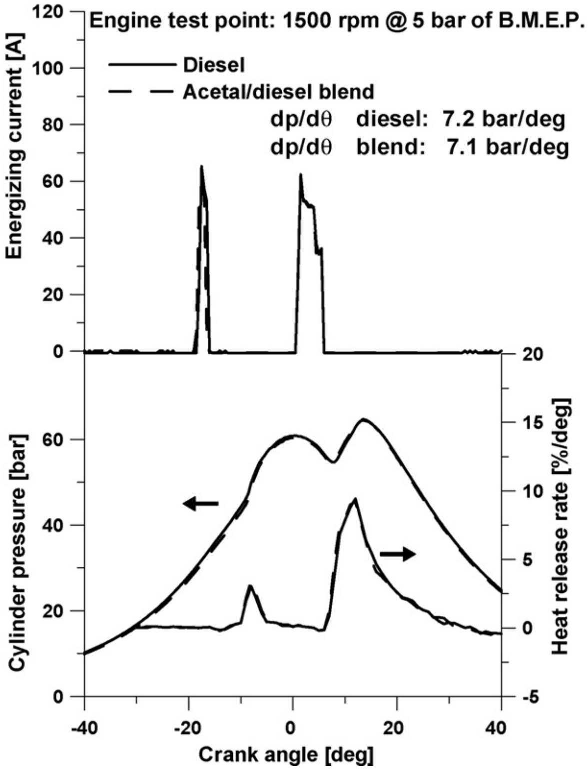

Fig. 7. Energizing current of electro-injector, cylinder pressure, rate of heat release of combustion and d*p*/d*ϑ* comparison for the two fuels in the 1500 rpm at 5 bar of BMEP engine operating point.

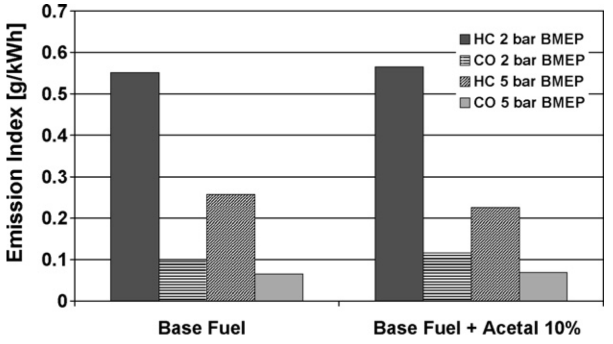

Fig. 8. HC and CO emissions comparison for the two fuels (diesel and acetal/diesel blend) in both engine operating points at 2 and 5 bar of BMEP.

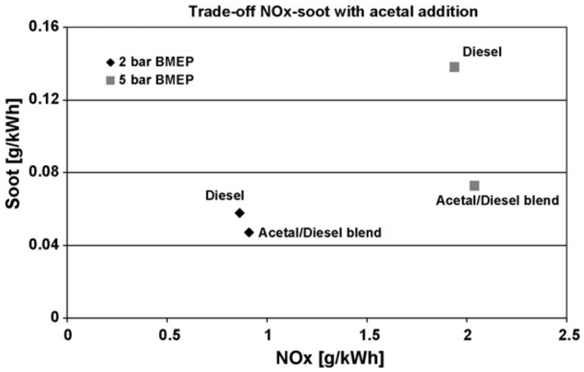

Fig. 9. NOx-soot trade-off for the two fuels (diesel and acetal/diesel blend) in both engine operating points at 2 and 5 bar of BMEP.

of heat release and the maximum pressure raise versus crank angle (d*p*/d*ϑ*) for both engine test points are plotted for the two fuels (diesel and acetal/diesel blend).

From the analysis of the figures, it can be observed that acetal does not affect the engine combustion behaviour because no significant difference between the two fuels were noticed.

In fact, at the same injection setting, as evidenced from the same energizing current signals, it corresponds a perfect overlapping of cylinder pressure and rate of heat release curves.

In addition, the maximum pressure rate versus crank angle is also labelled, evidencing no variation in maximum pressure rate, this last directly related to the combustion noise and so to the comfort aspect of the engine. Therefore, acetal addition shows a “transparent” effect on combustion behaviour and this is a promising result of the use of these kinds of additives.

At the exhaust of the engine, the effects of acetal addition were analyzed by means of gaseous and smoke emissions measurements. Fig. 8 shows the HC and CO emission values, while Fig. 9 reports NOx-soot trade-off. Nitrogen oxide and soot are the most incriminating pollutants at the exhaust of the diesel engine and their trends are typically opposite. Differently from the other pollutants, in Fig. 9 their values have been plotted as abscissas and ordinates in order to evidence the effect of acetal addition on both of them.

In terms of unburned gaseous emissions (Fig. 8), no significant variations were noted, as the differences reported in the same figure are inside the standard deviation of the measurement. On the contrary, in Fig. 9 is evident that the presence of oxygen in the fuel involves in a reduction of exhaust smoke and a slight increase of NOx emissions. This was an expected result, in agreement with previous studies on diesel oxygenated synthetic fuels reported in literature [22,23].

In fact, in modern diesel engines, many literature results indicate that NOx emissions are mainly sensible to exhaust gas recirculation (EGR) level rather than to fuel quality, while smoke is strongly dependent from the global oxygen content. Anyway the kind of oxygenate product can also play a significant role on soot emission reduction [22,23,27–30].

Table 6 reports the smoke emission percentage reduction offered by the blend of acetal with respect to the pure diesel fuel.

Fig. 10 compares the fuel consumption at the same engine torque (brake specific fuel consumption-BSFC) for the pure diesel and its blend at 10% of acetal in the two test operating points. The slight increase of BSFC using the blend is only due to the lower heat content of the additive with respect to the pure diesel fuel, with any detrimental effect of the acetal on the

Table 6
Smoke emission reduction in percentage of acetal/diesel blend with respect to the pure diesel fuel

Operating point	Smoke reduction (%)
1500 rpm at 2 bar BMEP	18
1500 rpm at 5 bar BMEP	48

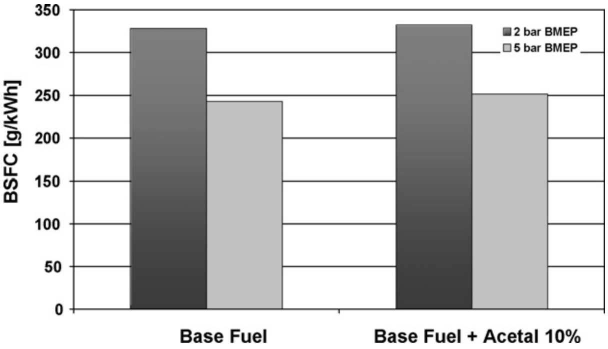

Fig. 10. Brake specific fuel consumption comparison for the two fuels (diesel and acetal/diesel blend) in both engine operating points of 2 and 5 bar of BMEP.

combustion efficiency as confirmed from the quite same values of unburned gaseous emissions using the two fuels (see again Fig. 8).

4. Conclusions

The present paper has described the preliminary characterization of an alternative synthetic oxygenated fuel for diesel engines obtainable by bio-ethanol. This last characteristic goes the product bio-derivable and so very interesting for CO_2 emission reduction in the atmosphere. The compound is the 1,1-diethoxyethane, briefly named acetal.

The *heterogeneization* of PFS acid polymers on pre-formed SiO_2 carrier by a simple impregnation technique does not affect the acidic properties of the bare PFS polymer, leading to very significant improvement in the surface area which allows for a full availability of the sulfonic acidic groups in acid-catalysed liquid-phase reactions. The suitability of PFS–SiO_2 catalysts for the synthesis of acetal has been ascertained. The catalysts result very active and selective towards the production of acetal, denoting also a good mechanical and chemical stability under the typical process conditions. The acetal yield obtained by the employment of PFS–SiO_2 catalysts result the highest than those reported in the literature using diverse solid-acid catalysts [2].

The product (1,1-diethoxyethane) was tested in a diesel engine as oxy-additive of a fossil diesel fuel, and its performance in terms of combustion behaviour and emission reduction were evaluated and compared with those of the pure diesel fuel.

The global analysis of the results has shown an insensitive effect on gaseous emissions (HC, CO and NOx) and a marked reduction of exhaust smoke [22,23,27–30]. Fuel consumption was slightly increased and linked with the total oxygen content of the blend.

Due to its too low flash point this product cannot be used in diesel vehicles without the adoption of adequate safety systems. Notwithstanding, the exploration of new alternative ways to produce "green" bio-derived oxy fuels, useful for pollutant emission reduction from internal combustion engines, appears very promising.

References

[1] R. McCormick, R. Parish, Advanced petroleum based fuels program and renewable diesel program: "Technical barriers to the use of ethanol in diesel fuel", Milestone Report NREL/MP-540-32674, National Renewable Energy Laboratory, (November 2001).
[2] M.R. Capeletti, L. Balzano, G. de la Puente, M. Laborde, U. Sedran, Appl. Catal. Gen. A 198 (2000) L1.
[3] Pat. Huls AG-DE 44 04 515 A1 (1995).
[4] R.A. Sheldon, Chem. Ind. (1997) 12.
[5] R.A. Sheldon, H. Van Bekkum, Fine Chemicals Through Heterogeneous Catalysis, Wiley VCH, Weinheim, 2000.
[6] A. Corma, H. Garcia, Chem. Rev. 103 (2003) 4307.
[7] A. Corma, M.J. Climent, H. García, J. Primo, Appl. Catal. 49 (1989) 109.
[8] R. Fang, G. Harvey, H.W. Kouwenhoven, R. Prins, Appl. Catal. Gen. A 130 (1995) 67.
[9] K. Garre, D. Akporiaye, J. Mol. Catal. A 109 (1996) 177.
[10] K. Smith, Z. Zhenhua, P.K.G. Hodgson, J. Mol. Catal. A 134 (1998) 121.
[11] Y. Ma, W. Wang, W. Jiang, B. Zuo, Appl. Catal. Gen. A 165 (1997) 199.
[12] D. Das, S. Cheng, Appl. Catal. Gen. A 201 (2000) 159.
[13] Q.L. Wang, Y. Ma, X. Ji, Y. Yan, Q. Qiu, Chem. Commun. (1995) 2307.
[14] R.D. Badley, W.T. Ford, J. Org. Chem. 54 (1989) 5437.
[15] G. Olah, P.S. Iyer, G.K. Surya Prakash, Synthesis (1986) 513.
[16] Pat. Degussa AG-DE 34 03 426 A1 (1985).
[17] G.A. Olah, NATO ASI Ser. C 444 (1994) 305.
[18] M.A. Harmer, W.E. Farneth, Q. Sun, Adv. Mater. 10 (1998) 1255.
[19] M. Alvaro, A. Corma, D. Das, V. Fornés, H. García, J. Catal. 231 (2005) 48.
[20] P.L. Antonucci, A.S. Aricò, P. Cretì, E. Ramunni, V. Antonucci, Solid State Ionics 125 (1999) 431.
[21] A.S. Aricò, V. Antonucci, M. Minatoli, N. Giordano, Carbon 27 (1989) 337.
[22] N. Del Giacomo, C. Bertoli, C. Beatrice, M. Migliaccio, C. Guido, "Potentiality of the modern engines fed by new diesel fuels to approach the future European emission limits", SAE Paper 2002-01-2826, (Reprinted in SAE 2002 Transactions "J. Fuels Lubricants" 111 (2002) 1767).
[23] Pat. BASF DE 0014 992 (1980).
[24] M. Uchida, Y. Aoyama, N. Eda, A. Ohta, J. Electrochem. Soc. 142 (1995) 463.
[25] F.W. Billmeyer, Textbook of Polymer Science, 3rd ed., Wiley–Interscience Publication, 1984, p. 276.
[26] G. Alberti, M. Casciola, Annu. Rev. Mater. Res. (2003) 129.
[27] J.B. Heywood, Internal Combustion Engine Fundamental, McGraw-Hill, Inc. ISBN0-07-028637-X (1989).
[28] C. Beatrice, C. Bertoli, N. Del Giacomo, Environ. Combust. Technol. 1 (1997) 205.
[29] Pat. Daimler Benz DE 29 11 411 A1 (1980).
[30] Pat. Daimler Benz DE 31 36 030 A1 (1983).